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Gas-Liquid Interfacial Area Determination for a Turbine Agitated Reactor

J. A. BOSSIER, III, R. E. FARRITOR, G. A. HUGHMARK, and J. T. F. KAO

Ethyl Corporation
Baton Rouge, Louisiana 70821

Gas absorption accompanied by a very rapid chemical reaction has been used as a method for the determination of interfacial area between gas and liquid phases. Methods used are oxidation of aqueous sodium sulfite solutions in the presence of a catalyst and carbon dioxide absorption in solutions of alkalis and amines. Visual observation of gas dispersions in mechanically agitated liquid systems indicates that the interfacial area in typical organic liquids is much greater than in aqueous systems. Thus there is an incentive to develop a chemical method for interfacial area determination for organic liquids. Selection of the system must consider the following requirements:

1. The reaction of gas and liquid must be very fast so as to provide a boundary layer reaction. Van Krevelin and Hoftyzer (1953) and Yoshida and Miura (1963) have shown that the theory of gas absorption with fast first-order chemical reaction in the liquid phase results in the apparent mass transfer coefficient

$$k_L^* = \sqrt{kD} \tag{1}$$

and $k_L^*/k_L > 2$. Calderbank (1959) reports typical values of k_L for agitated vessels are in the range of 0.01 to 0.1 cm/s and liquid phase diffusivity for gases is of the order of 3×10^{-5} cm^2/s so the kinetic rate must be greater than 10^3 s^{-1} to provide a boundary layer reaction.
2. The reaction between gas and the reacting liquid phase component must be capable of being represented by one first- or second-order reaction.
3. No gaseous reaction products are generated which will dilute the reactant gas phase and provide mass transfer resistance in the gas phase.
4. The reacting liquid phase component must have negligible vapor pressure at reaction temperature so that the reaction can be confined to the liquid phase.

This is a difficult list of qualifications to meet. Aluminum alkyls provide very fast reactions with oxygen to form aluminum alkoxides so C_{10} aluminum alkyl was selected. This material meets all of the requirements for interfacial area determination and can be mixed with nonreacting liquids to provide a range of liquid viscosity. The oxidation does have a disadvantage in the high heat of reaction, approximately 180 k cal/g mole of oxygen. The reaction proceeds too fast to follow with liquid phase analysis so a system was designed to determine the rate of oxygen consumption.

EXPERIMENTAL APPARATUS AND PROCEDURE

A 4-in. diam. pyrex vessel was used for all of these experiments. Four stainless steel baffles, each with a width of one-tenth of the tank diameter, were used. The impeller was 2-in. diam. with six flat blades. Liquid depth was equal to the vessel diameter. The impeller was driven by a magnetic drive which was controlled by a Cole-Parmer standard Servodyne. Oxygen was supplied from a 1.43-liter container fitted with a PP type SR-4 pressure cell and a pressure gauge. A recorder was used for the output signal from the pressure cell. The pressure cell has a maximum error of ¼% over the calibrated pressure range. The unit was calibrated before each run over a range of about two atmospheres so the maximum error in pressure was about 4 mm Hg.

Experimental procedures were as follows: The reactor system was leak tested at full vacuum from a vacuum pump. The system was pressurized with nitrogen and then the solvent was charged. The alkyl was then added under the liquid surface so that it would go to the bottom of the reactor. Initial alkyl concentration was 30% by volume. The nitrogen was evacuated and an absolute pressure of about 5 mm Hg was maintained while the liquid was degassed. This was accomplished by freezing and thawing the liquid phase under vacuum. Two freezing cycles appeared to remove the dissolved gas. The reactor system was purged with 99.5% oxygen under vacuum and was then pressurized to about 100 mm Hg pressure with 99.999% oxygen from the pressure cell bomb without agitation. A mercury manometer was used for pressure readings on the reactor. The impeller was then set at the desired speed and oxygen was fed from the pressure cell bomb to maintain a constant pressure. Pressure in the bomb as a function of time was recorded by the recorder. After about 10% oxidation of the alkyl, the oxygen was shut off and agitation was continued until a constant pressure reading was observed in the reactor. Residual inerts pressure was observed to be 10 to 20 mm Hg and this was found to appear linearly during the oxidation. The system could then be evacuated and another run could then be made. This procedure was repeated until about 50% of the oxygen had been added to produce the alkoxide. Total oxygen consumption was recorded so that the alkyl concentration could be calculated for the initial condition of each run.

The experimental data were obtained with a single impeller positioned at one-fourth of the liquid depth. This impeller position was observed to provide excellent gas dispersion in the liquid phase at a speed of about 900 rev./min. by entrapment of gas from the gas space of the vessel. Gas was not sparged into the liquid.

Tetradecane, *p*-xylene, and Nujol were used as diluents for the alkyl. These have low vapor pressure at the nominal reaction temperature of 20°C and do not react with the alkyl. Molecular sieves were used to dry the solvents before use.

Heat generated from the reaction was greater than could be removed through the reactor walls. A dry ice-isopropanol bath was used for external cooling. Reactor contents were cooled to about 7°C before oxygen addition, and then the bath was maintained on the reactor during the reaction period. Reactor temperature increased 20° to 30°C during the reaction with tetradecane and *p*-xylene mixtures. Oxygen reaction with the Nujol mixture was slow enough that a constant temperature could be maintained.

KINETIC RATE

The chemical method for interfacial area determination requires the kinetic rate for the reaction. The kinetic rate for C_{10} aluminum alkyl oxidation was not known so it was necessary to obtain this experimentally. This was done with the use of impeller speeds that provided a stirred but unbroken gas-liquid interface. Thus the interfacial area was the cross-sectional area of the reactor and the oxygen absorption rate was determined by the same procedure as was used for interfacial area determination. The oxygen rate was low enough with this limited interfacial area so that constant temperature could be maintained with the cooling bath. If the reaction conditions are pseudo first order, the equation

$$k_L^* = \sqrt{kD_0C_A} \qquad (2)$$

is applicable. If the reaction is not pseudo first order, the method of Brian, Hurley, and Hasseltine (1961) must be used which requires the mass transfer coefficient without chemical reaction for identical conditions to that of the reaction. Table 1 summarizes the experimental mass transfer coefficients without reaction and with an unbroken interface.

TABLE 1. UNBROKEN INTERFACE WITHOUT REACTION

System	Temperature, °C	Rev./min.	k_L, cm/s
Tetradecane + alkyl, N_2	50	100	0.0085
Tetradecane + alkyl, N_2	50	200	0.017
Tetradecane + alkyl, N_2	50	290	0.0235
Tetradecane, O_2	23	100	0.0125
Nujol, N_2	50	300	0.0097
Nujol, N_2	10	500	0.0043

TABLE 2. C_{10} ALUMINUM ALKYL OXIDATION RATE

System	Temperature, °C	k, liters/g mol-s
p-xylene	23	1.4×10^4
Tetradecane	50	5.5×10^4
Tetradecane	23	1.9×10^4
Tetradecane	10	6400
Nujol	23	3890

Analysis of the kinetic data showed that the pseudo first-order analysis was satisfactory. Table 2 summarizes the kinetic data.

The *p*-xylene and tetradecane data are represented by the equation

$$k = 9.3 \times 10^{10} e^{-9200/RT}$$

Apparent mass transfer coefficients with reaction are from 10 to 50 times the mass transfer coefficient without reaction so this is obviously a boundary layer reaction at these conditions.

OXYGEN SOLUBILITY IN THE LIQUID PHASE

Oxygen solubility in *p*-xylene, tetradecane, and Nujol were experimentally determined for use in the interfacial area calculations. The equipment for interfacial area determination was modified to eliminate the oxygen pressure container, and the pressure cell was connected directly to the reactor. The procedure was to degas the solvent, pressurize the system without agitation, and then observe the change in pressure with agitation. Solubility as Henry's law constants at 23°C are 1.16×10^{-5} for *p*-xylene, 1.3×10^{-5} for tetradecane, and 0.94×10^{-5} for Nujol with units of g mol/liter-mm Hg. Schläpfer et al. (1949) report oxygen solubility in *p*-xylene as 1.2×10^{-5} g mol/liter-mm Hg at 23°C.

INTERFACIAL AREA

Gas-phase mass transfer resistance is negligible because this phase is essentially a pure gas. A two-bladed impeller was placed on the agitator shaft so that this impeller stirred the gas phase to minimize local inerts buildup. Liquid phase mass transfer is represented by the equation

$$N = k_L a \Delta C \qquad (3)$$

For a boundary layer reaction, $k_L = k_L^*$, and the oxygen concentration is zero in the bulk liquid phase so $\Delta C = HP$. Substitution and combination with Equation (2) gives the equation for interfacial area with a pseudo first-order reaction.

$$a = \frac{N}{\sqrt{kD_0C_A}\ HP} \qquad (4)$$

Viscosity of aluminum alkyl solutions was determined with a Haake Model B/BH Falling Ball Viscosimeter. Diffusivity of oxygen in *p*-xylene and tetradecane solutions were estimated from the data of Hayduk and Cheng (1971) for CO_2 diffusivity as a function of liquid viscosity. Oxygen diffusivity in the Nujol solution was estimated as a kinematic viscosity function from methane diffusivity in white oil from the data of Reamer et al. (1956).

The oxygen absorption data are such that the reaction period can be divided into increments and interfacial area can be calculated for each increment with consideration of the alkyl concentration, oxygen partial pressure, and temperature. Table 3 presents a summary of the interfacial area results.

An objective of this work was to compare interfacial area for organic and aqueous liquid systems. Reaction of carbon dioxide and aqueous caustic as a method for interfacial area determination is described in a review paper by Danckwerts and Sharma (1966). The interfacial area determination apparatus was used with 99.8% CO_2 and 0.84 N NaOH aqueous solution. A constant temperature of 23°C was maintained. The result of this experiment is also included in Table 3. Interfacial area for this system is shown as about 25% of that for *p*-xylene and tetra-

TABLE 3. INTERFACIAL AREA

System	Rev./min.	D_0 $\times 10^5$ cm^2/s	Viscosity, cp	a cm^2/cm^3
p-xylene-O_2	850	4.8	1.2	9.0
Tetradecane-O_2	850	3.3	3.6	10.8
Nujol-O_2	850	1.2	71	2.33
Aq NaOH-CO_2	900	1.8	1.05	2.3

TABLE 4. OXYGEN ABSORPTION DATA

Liquid phase	k_La 1/s	k_L cm/s	$\frac{\nu}{D}$
p-xylene	0.85	0.094	313
Nujol	0.0115	0.0077	69,000
1 N Na_2SO_4	0.173	0.075	580
Water	0.145		

decane. Oxidation of aqueous sodium sulfite with copper catalyst has been used extensively for interfacial area determination. Westerterp, van Dierendonck, and de Kraa (1963) used this system to obtain interfacial area for sparged, agitated reactors. De Waal and Okeson (1966) and Linek and Mayrhoferová (1969) have published papers which state that the copper catalyzed oxidation is not applicable to interfacial area determination. The experimental conditions described by Westerterp et al. were used for a run with the reactor described in this paper. Air was used and the reaction was followed with an iodimetric titration. The reaction obviously proceeded very slowly in comparison to the prior reactions and an interfacial area of 0.2 cm^2/cm^3 was calculated. Use of air raises a question as to the oxygen concentration of the gas in contact with the liquid phase so a gas sample was taken from the liquid phase and analyzed to show 17% oxygen. It is apparent that the copper catalyzed oxidation is not applicable for interfacial area determination because the reaction is too slow to be a boundary layer reaction.

MASS TRANSFER COEFFICIENTS

The apparatus for determination of interfacial area can also be used for determination of absorption rates or k_La in the solvents. With similar experimental conditions the interfacial area data and k_La data can be utilized to obtain mass transfer coefficients. Table 4 shows the oxygen absorption data and calculated mass transfer coefficients. Conditions were 900 rev./min. impeller speed and ambient temperature.

The mass transfer coefficient for the sodium sulfate solution assumes that the interfacial area is that determined for the CO_2-NaOH solution. The coefficients obtained for p-xylene and the aqueous solution compare with values of about 0.08 cm/s for large bubbles and 0.02 cm/s for small bubbles reported by Calderbank (1959) for this diffusivity.

Depletion of reactant at the liquid phase interface is a potential source of error with the chemical method for interfacial area determination. The concentration gradient of the liquid phase reactant can be estimated from the oxygen flux at the interface, liquid phase mass transfer coefficients, and the interfacial area. Calculated concentration gradients showed differences of 1.5% and 3% between interface and bulk concentration for oxygen-aluminum alkyl and CO_2-NaOH solution respectively. This represents a negligible correction for the pseudo first-order mechanism represented by Equation (4).

CONCLUSIONS

Oxidation of C_{10} aluminum alkyl in organic solution represents a satisfactory method for determination of interfacial area in gas-organic liquid systems. Absorption and reaction of CO_2 in aqueous NaOH solution also appears to be a satisfactory interfacial area method. At similar agitation conditions, the mass transfer coefficients appear to be about the same for typical organic liquids and aqueous NaOH solution. Interfacial area for the organic liquid system is about four times that of the aqueous system. The sulfite oxidation with copper as a catalyst appears to be a bulk phase reaction and is not applicable for interfacial area determination.

NOTATION

a = interfacial area per unit volume of liquid
C_A = aluminum alkyl concentration
ΔC = liquid phase concentration gradient
D = molecular diffusivity
H = Henry's law constant
k = kinetic rate
k_L = liquid phase mass transfer coefficient
k_L^* = apparent mass transfer coefficient with chemical reaction
N = molar flux-mass transfer
P = reactant gas pressure
ν = kinematic viscosity

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